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ON THE MECHANISM OF COLD-FLAME COMBUSTION

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[Table and figures referred to are appended.]

The application of a thermo-couple coated with $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$, the heating of which depends on the catalytic recombination of H atoms, has made it possible to detect and determine quantitatively the concentration of atomic hydrogen in H_2 [1] and CO [2] flames. By means of this method the presence of atomic H and its concentration in C_2H_2 flames were established with a high degree of probability C_2H_2 [3]. Our attempts to apply the method to other hydrocarbons flames was unsuccessful. It was impossible to obtain a stationary flame with a temperature sufficiently low to prevent a heterogeneous reaction on the surface of the catalyst. For this reason we turned our attention to the study of cold flames, where the absence or presence of atomic H is of considerable interest from the standpoint of the flame mechanism.

The mechanism of cold flames observed with hydrocarbons (excluding methane), aldehydes (excluding formaldehyde), and ethers differs from the mechanism of hot flames of these substances. The hot flames are characterized by active centers consisting of free atoms and simple radicals [4]. All experimental data pertaining to reaction kinetic in cold flames and to the analysis of their reaction products as well as the results of spectroscopic analysis indicate that the active substances in cold flames are peroxides and compounds of the complex radical type.

The results of Gaydon [5] based on the study of the process $\text{NO} + \text{O} \rightarrow \text{NO}_2 + h\nu$ lead to the same conclusion. Gaydon's experiments showed that atomic oxygen is not present in the inner cone of a hydrocarbon flame. The analysis of the reaction products in the inner cone indicates that the mechanism of the reaction

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taking place there has certain properties common to cold flames. This raises a doubt as to the validity of the mechanism of low-temperature oxidation of hydrocarbons and aldehydes proposed by Elbe and Lewis [6]. The negative results obtained by the present authors in their attempt to detect atomic hydrogen in $(C_2H_5)_2O$ and CH_3CHO flames also lead to the conclusion that atomic gases are not present in cold flames.

The experimental methods we employed do not differ from those used in the study of hot flames. The oxygen enters the displacement flask from the gasometer and the fuel vapor from a vessel filled with liquid fuel. The rate of delivery is regulated by valves. The gasometer shows the consumption of oxygen and the fuel level in the vessel indicates the consumption of fuel. The compositions α of the combustible mixtures are determined by means of the following formulas:

$$\alpha = \frac{1}{6} \frac{V_{O_2}}{V_{eth}}, \quad \alpha = \frac{2}{5} \frac{V_{O_2}}{V_{ald}}$$

where V_{O_2} , V_{eth} , and V_{ald} are the volumes of oxygen ether vapor and aldehyde vapor reduced to standard conditions.

In the various experiments with ether, the maximum temperature of the flame was 210-360° C, the pressure in the reaction vessel was 15-50 mm of mercury and α was 0.17-0.73. The maximum flame temperature in the case of aldehyde (one experiment) was 420° C with a pressure of 50 mm and $\alpha=0.39$. The experiments were conducted in such a way that after a stationary flame was obtained (in the stream) the temperature was measured (by means of both thermocouples) at various distances l from the heated end of the combustion vessel ($l=0, 1, 2, \dots, 10$ cm). Since the temperature increment ΔT , which was measured by the difference between the reading of the coated thermocouple and that of the control thermocouple, was anticipated to be quite small for the cold flame and since the flow in the stream was not uniform, it was necessary to introduce corrections. These were made by taking a second set of temperature readings with the oxygen replaced by argon. The difference $\Delta T = (\Delta T)_{O_2} - (\Delta T)_{AR}$ was taken as the actual temperature increment.

Our results showed that within the limits of experimental error, which is 2° C, the value of ΔT is equal to zero. However, we cannot conclude from this that atomic hydrogen is completely absent in a cold flame. To substantiate such a conclusion, it is necessary to evaluate the reaction velocity in the cold flame since the concentration of the H atoms is directly related to the reaction velocity.

Our attempts to evaluate the magnitude of the reaction velocity from fuel consumption produced no reliable results due to the large errors incurred in measuring relatively small volumes of liquid which vary little in magnitude one from another. Therefore, we used an indirect method which we shall describe below.

The temperature of a stationary flame is directly related to the quantity $Q_V \gamma$ (Q is the molecular heat of reaction, γ the percentage of complete combustion, V the volume of fuel vapor delivered per unit time) which is a measure of the quantity of liberated heat. Figure 1 shows the flame temperature t as a function of $Q_V \gamma$ based on our measurements. The values of temperature in Figure 1 are the averages of readings at $l=4$ cm and $l=6$ cm. If we assume that the relation between the temperature of the cold flame and the amount of heat liberated in it is the same as for the case of CO, we can compute the extent of combustion (γ) from the following equation:

$$\gamma_{eth} = \frac{Q_{co} V_{co}}{Q_{eth} V_{eth}} \gamma_{co} \quad (1)$$

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which is valid for the same temperature increments in the flame and the same reaction tube wall temperature. In each case, the temperature of the wall was assumed to be equal to that measured with $\gamma=0$ (no flame). The heat of combustion of carbon monoxide is $Q_{CO}=66,760$ cal per mole while the heat of combustion of diethyl ether is $Q_{eth}=660,300$ cal per mole. It should be pointed out that since carbon dioxide and water are far from being the sole products formed in the cold ether flame, the actual heat of combustion of ether under conditions of a cold flame must be less than the heat of its complete combustion.

Thus the percentage of ether which is burned (γ_{eth}) varies from 3.35 to 8.63%. The curve showing the temperature as a function of $10 \gamma_{eth} v_{eth} \left(\frac{Q_{eth}}{Q_{CO}} \right)$ which is presented in Figure 2 is similar to the analogous curve for CO. It follows that our evaluation of the percentage of burned ether is correct. A similar evaluation for the case of acetaldehyde burning under similar conditions gives us $\gamma \sim 22\%$.

If we assume that for equal reaction velocities (γV) the concentrations of atomic hydrogen in cold flames and in the CO flame are the same, we can compute the corresponding values of temperature increments ΔT for cold flames provided we know the value of γV for each experiment with ether and aldehyde and the maximum temperature increment ΔT (in the center of the combustion zone) as a function of γV for the CO flame. The results of such a calculation are presented in Table 1.

We can see that the calculated values of ΔT are several times greater than the measurement error (20). Since our measurements indicated that within the limits of experimental error the actual temperature increment is zero, we may conclude that atomic hydrogen is either absent in cold flames of diethyl ether and acetaldehyde or else its concentration is considerably lower than in a hot carbon monoxide flame (with the same reaction velocity). If we assume that the heat balance of thermo-couples in cold flames approaches the heat balance in the CO flame, and if we make use of the ratio

$$\frac{\bar{P}_H}{P} = \frac{\Delta T_{max}}{80,000}$$

where \bar{P}_H is the partial pressure of atomic hydrogen, we find, by making $\Delta T_{max} \leq 20$, that

$$\frac{\bar{P}_H}{P} \leq 0.0025\%$$

Regardless of which of the two possible conclusions concerning the concentration of H atoms in cold flames is valid, we must conclude that the H atoms, even if they are present in cold flames, do not play the same important role that they do in the mechanism of hot flames.

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- [Table and figures follow.]

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Table 1.

Ether					
Expt No	γV	ΔT	Expt No	γV	ΔT
8	0.095	8	23	0.051	3.5
9	0.079	6	24	0.095	8
10	0.073	5.5	25	0.126	10
14	0.056	4	26	0.082	6
15	0.063	4.5	28	0.071	5.5
16	0.084	6.5	29	0.071	5.5
17	0.082	6	30	0.068	5
18	0.082	6			

Aldehyde

2 0.169 13

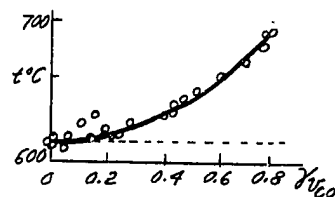


Figure 1

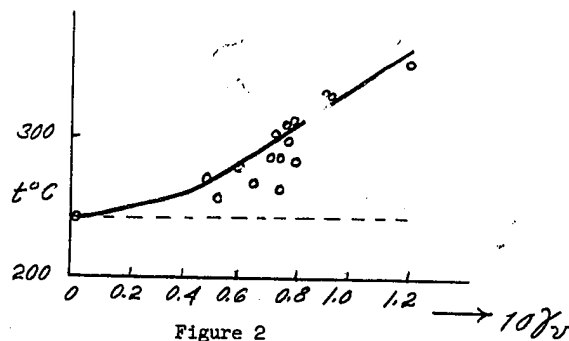


Figure 2

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